Probing the local electronic structure in the H induced metal-insulator transition of Y

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INTRODUCTION

The interest in the optical properties of the lanthanide hydrides increased significantly with the discovery of the hydrogen induced optical switching, causing metallic Y film to become transparent upon H loading [1]. Although this metal-insulator (M-I) transition is conceptually simple, the details of the changes in the electronic structure is not fully understood. The previous understanding of the transition was based on band structure calculations [2], where a band gap of ~1.5 eV was obtained. Recent state of the art band structure calculations failed, however, to reproduce these results [3,4]. Furthermore, theoretical calculations focusing on the relation between the crystallographic and the electronic structure[5] are found to be inconsistent with the interpretation of recent experimental results [6,7]. Optical transition probabilities depend on matrix elements for electric dipole transitions between occupied and unoccupied states, which in turn depend on the local symmetry [5]. Accurate knowledge of the crystallographic structure is thus essential for theoretically establishing the correct mechanism for the changes in the optical properties upon hydrogen loading.

Here we explore the density of states close to the Fermi level by soft X-ray emission and absorption spectroscopy, as well as by first principles calculations, and discuss the intrinsic changes of the electronic structure upon hydride formation. Thereby, we attempt to address the contribution of the metallic states to the optical and electric properties of the yttrium hydrides. The existence of a direct band gap for the trihydride state will be demonstrated, as well as the formation of a hydrogen induced sub-band below the Fermi level. All the experiments were performed on well characterised single crystal films.

Soft X-ray emission spectroscopy (SXES) allows direct probing of the site specific angular momentum components for the electronic energy distribution, furthermore due to the relatively large penetration depth of the X-rays, it yields information on bulk properties. Thus, the use of soft X-ray absorption spectroscopy (SXAS) in combination with SXES allows the determination of the DOS of the occupied and the unoccupied part of the valence band. Hence the appearance of a band gap for e.g. insulators can be obtained and the details of the electronic structure in the vicinity of the Fermi level can be investigated.

EXPERIMENT

The samples were grown using MBE techniques described in detail elsewhere [8]. Niobium is used as a buffer to prevent reaction between the rare earth metals and the oxide substrate. The epitaxial relationships at the sapphire/niobium interface are (1120)S//(110)Nb, [0001]S//[111]Nb and at the niobium/yttrium interface (110)Nb//(0001)Y, [001]Nb//[1120]Y.

The samples were charged with hydrogen in an UHV-based hydrogen reactor. The samples were heated to elevated temperatures during the hydrogen exposure, to further reduce the strain induced defect formation. After the loading, the samples were analysed by X-ray diffraction (θ-2θ). A single Bragg peak corresponding to YH_2 was observed in the dihydride sample with an fcc lattice parameter a=0.5224 nm. The bulk value at room temperature is 0.52095 nm [9]. The lattice parameter is known to decrease as the H/Y atomic ratio exceeds 2. The trihydride sample exhibits a dominating YH_3 Bragg peak (hcp lattice parameter c=0.6614 nm, cf. bulk c=0.6659 nm [10]) and a small YH_2 peak (fcc a=0.5210 nm). The ratio of the dihydride and the trihydride phases was estimated to be below 1/300.

The experiments were performed at 7.0.1 undulator beamline at the ALS, LBNL [11]. In the present work the Y $M_{4,5}$ soft X-ray emission was recorded by a grazing incidence grating spectrometer with a resolution of 0.35 eV [12]. The monochromatised synchrotron radiation beam impinged at 60° from the sample surface normal and the emission was recorded at right angle with respect to the incoming beam, and parallel to the polarisation of the beam. The excitation energy bandpass was < 0.1 eV and the X-ray emission energy scale was calibrated and related to the excitation energy scale using the elastic (recombination) peaks.

RESULTS AND DISCUSSION

Figure 1 depicts the Y $3d_{5/2}$ - $4p_{3/2}$ emission spectra of the yttrium metal, yttrium dihydride, and yttrium trihydride, respectively. The width of the transitions are broader in the hydrides than that of the Y metal and shifted towards lower photon energies. The shift originates from the decreased energy separation of the involved levels. If the binding energy of the $3d$ level increases, the shift of the $4p$ level has to be of the same sign and larger. On the other hand, if the binding energy in the $3d$ level decreases, the shift of the $4p$ level can be of the same sign, but smaller. X-ray emission measurements on a series of Y compounds [13] revealed large shift of inner $1s$-$2p$ and $1s$-$3p$ transition on Y^{3+} ions with respect to those of the Y metal. In the present case, the Y $3d_{5/2}$ - $4p_{3/2}$ line shifts to lower energies, which is consistent with an increased electron charge at the Y sites. When electron charge is added to a site of an atom,

Figure 1. Y $3d_{5/2}$ - $4p_{3/2}$ inner transitions of Y, YH_2 and YH_3.

decreased binding energy of core electrons is expected (based on Coulomb interaction in the one-electron picture, see for example Ref. [13]). Thus, if the formation of the hydride increases the electron charge at the yttrium sites, one would expect the $3d$-$4p$ X-ray transition to be shifted towards lower photon energies, which is indeed observed.
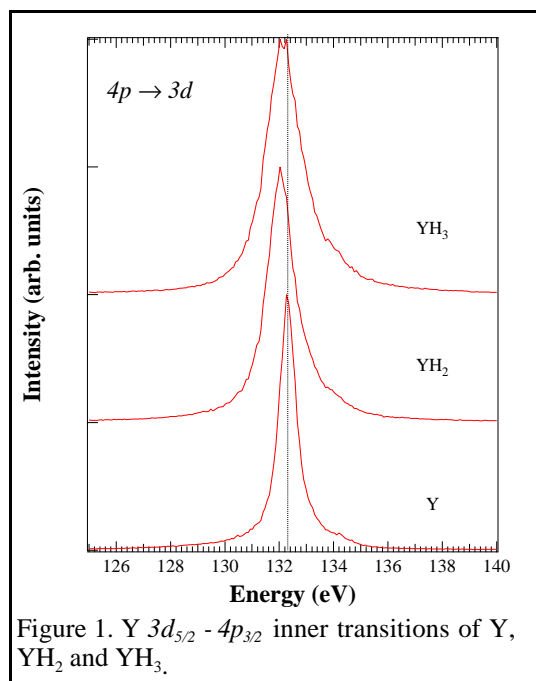
Figure 2 shows the valence-core SXES spectra of the three samples along with the corresponding soft X-ray absorption spectra (SXAS) recorded in fluorescence yield mode. The emission spectra were all normalised with respect to the integrated intensity of the $3d_{5/2}$ - $4p_{3/2}$ transitions (Figure 1). The $M_{4,5}$ emission reflects the p character partial DOS, as the core state is of d symmetry. Since yttrium metal should have weak $5p$ character, the intensity is expected be low, in accordance with the observations (the free Y atom does not possess $5p$ electrons, whereas in the solid, $5p$ states are induced by hybridisation). A sharp edge is observed at the top of the valence band in Y, a feature which is identified as the Fermi level (at 156.0 eV). The SXAS shows an onset at this energy, which implies an overlap between the valence band and the lowest part of the conduction band. Thus, the absorption-emission compound spectrum shows the unbroken density of states crossing the Fermi level, reflecting the metallic character of Y.
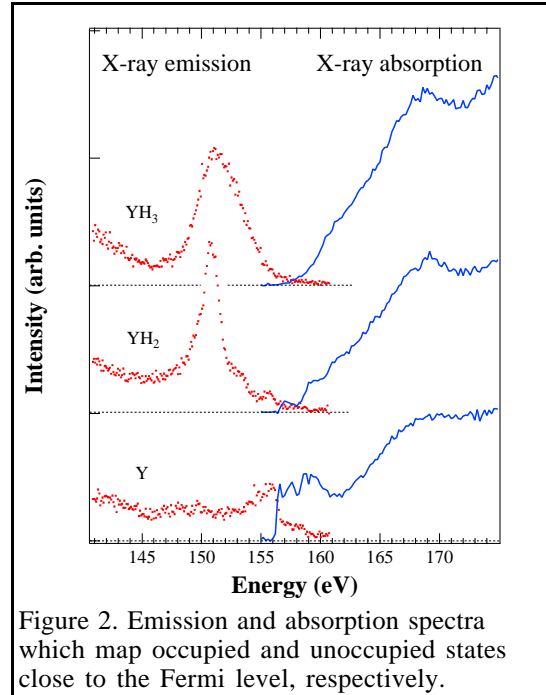

Figure 2. Emission and absorption spectra which map occupied and unoccupied states close to the Fermi level, respectively.

A substantial change is observed in the X-ray emission with increasing hydrogen content, as seen in Figure 2. The total intensity (normalised to the $3d$-$4p$ inner-core transition) increases considerably, and a strong feature appears at around 6-7 eV below the Fermi level. This observation is in agreement with a general behaviour of transition metal hydrides, in which the hydrogen and the host lattice form a sub-band below the Fermi level [14]. The trihydride spectrum displays a clear reduction of the DOS in the region corresponding to the Fermi surface of the metal, resulting in a band gap with the estimated width of 2.5 eV.

Symmetry and anisotropy induced intensity enhancement are expected to cancel by the normalisation to the $3d$-$4p$ transition. Thus, the $M_{4,5}$ X-ray emission results supports the view of hydrogen as electron donor, which is in line with the interpretation of the core-to-core spectra discussed above. These findings are in agreement with studies of the electronic structure of Y hydrides by positron annihilation [15,16] which also is a bulk sensitive technique.

In summary, the results show a hydrogen induced band-gap in the trihydride phase of Y. The obtained DOS are in qualitative and semiquantitative agreement with calculations of the transition probabilities. A formation of a sub-band some eV below the Fermi level are observed, and the results strongly support the protonic-like type of bonding of H.

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